

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 August 2005 (25.08.2005)

PCT

(10) International Publication Number
WO 2005/077990 A1

(51) International Patent Classification⁷: **C08F 4/654**,
10/00

(21) International Application Number:
PCT/IN2004/000043

(22) International Filing Date: 16 February 2004 (16.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **RELIANCE INDUSTRIES LIMITED** [IN/IN]; Maker Chambers IV, Nariman Point, Mumbai 400 021, Maharashtra (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BHADURI, Sumit** [IN/IN]; Reliance Industries Limited, Swastik Mills Compound, Sion-Trombay Road, VN Purav Marg, Chembur, Mumbai 400 071, Maharashtra (IN). **GUPTA, Virendra, Kumar** [IN/IN]; Reliance Industries Limited, Swastik Mills Compound, Sion-Trombay Road, VN Purav Marg, Chembur, Mumbai 400 071, Maharashtra (IN). **SARMA, Krishna** [IN/IN]; Reliance Industries Limited, Swastik Mills Compound, Sion-Trombay Road, VN Purav Marg, Chembur, Mumbai 400071, Maharashtra (IN).

(74) Agents: **JHUNJHUNWALA, Ram, N.** et al.; Khaitan & Co, Meher Chambers, 4th & 5th Floor, R K Marg,, Ballard Estate,, Mumbai 400 038, Maharashtra (IN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,

KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYTIC SYSTEM FOR POLYMERISATION OF LOWER ALPHA ALKENE.

(57) Abstract: Catalytic system for polymerisation of lower alpha alkene including a selectivity control agent which consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R) - dihydroxy-butane-1,4-dicarboxylic acid or (2-S, 3-S)-dihydroxybutane- 1,4-dicarboxylic acid. The molar ratio of the optically pure isomers of the tartrates to titanium being.0375 to 1.5.



WO 2005/077990 A1

TITLE OF INVENTION

Catalytic system for polymerisation of lower alpha alkene.

5

This invention also relates to process for the preparation of the catalytic system and process for the polymerisation of lower alpha alkene using the catalytic system.

10 BACKGROUND ART

Polymers of lower alpha alkene or olefins such as ethylene, propylene or 1-butene find applications in the manufacture of a variety of articles including plastic bags or sheets or automobile parts. Of particular interest in polymer production is polypropylene with a high degree of isotacticity ie the extent of orientation of the methyl groups in the polymer in the same direction, which shows high crystallinity. Polymerisation of lower alpha alkene such as ethylene or propylene involves reacting the monomer with a catalyst under polymerisation conditions. The early polymerisation catalysts were of relatively low activity and the polymers formed contained significant amounts of the catalyst residues, which had to be removed by deashing steps. The more recent alpha alkene polymerisation catalysts are of two types viz single site metallocene and non-metallocene catalysts and heterogeneous solid catalysts. The single site catalysts comprise metallocenes or co-ordination complexes of transition metals and a cocatalyst such as methyl aluminoxane and produces polymer of low polydispersity.

25

Heterogeneous solid catalysts are the most commonly used catalysts, especially in the bulk production of polyethylene or polypropylene due to their high

activity and ease of operation. These catalysts are sometimes referred to as Ziegler – Natta catalysts after the name of the inventors (Ziegler et al US Patents Nos 3,903,017; 4,063,009 and 4,125,698 and Natta et al US Patents Nos 3,197,452 and 3,957,743). Several improvements in terms of activity of the catalyst as measured by the amount of polymer produced per unit weight of catalyst and selectivity of the catalyst usually measured for polypropylene by measuring the amount of xylene soluble fraction have since taken place [Chapter 1 (by Brian L Goodall) and Chapter 9 in "Polypropylene and other Polyolefins; Polymerization and Characterization" edited by Ser van der Ven, Elsevier, New York, 1990].

Heterogeneous solid catalysts for polyethylene and polypropylene comprise a procatalyst and a cocatalyst and optionally an external electron donor or selectivity control agent (SCA). For polypropylene with high isotacticity one of the components of the procatalyst is an internal electron donor which works in tandem with the optional SCA. The procatalysts are synthesized by chlorination of an organomagnesium compound such as magnesium ethoxide with a chlorinating agent such as titanium tetrachloride in a hydrocarbon or halohydrocarbon solvent such as toluene or chlorobenzene in a multi step reaction so that simultaneous fixing of titanium tetrachloride on magnesium chloride occurs. The internal electron donor is added during the preparation of the polypropylene procatalyst. The procatalyst for polypropylene may also be prepared by milling together anhydrous magnesium chloride with titanium tetrachloride and an internal electron donor.

European Patent No 336,545 of Bailly et al describes the optional use of aromatic esters such as ethyl benzoate, methyl paratoluate or dibutyl or diisobutyl phthalate as electron donors. US Patent No 4,107,414 of Giannini et al, describes the

use of ethyl benzoate, 1,2, dimethoxy benzene or tetrahydrofuryl methyl ether as internal electron donors and esters of oxygenated organic and inorganic acids as external electron donors. Esters of aromatic acids are reported to give best results. US Patent No 4,522,930 of Albizzati et al, describes the use of ethers, ketones, lactones, esters and compounds containing nitrogen phosphorous and/or sulfur atoms as internal electron donors, and compounds with Si-OR, Si-OCOR bonds as SCA. Shamshoum in European Patent No 0605380A2 also reports the use of alkoxy silanes as SCA with commercial Ziegler-Natta catalysts. Use of diether compounds as effective electron donors has been described in European Patent No 728,741 of Morini et al, European Patent No 361,949 of Scordamaglia et al and European Patent No 362,705 of Barbe et al. Use of diethers with alkoxysilane external donors is described by Iskola et al in US Patent No 5,869,418. Use of diethers as internal electron donors eliminating the need of SCA is reported in US Patent No 5,068,213 of Albizzati. US Patent No 5,891,817 of Shamshoum et al describes the use of di-n-alkyl di-methoxy silanes as SCA in combination with diesters of phthalic acid as internal electron donors. US Patent No 6,451,726 of Tagge describes the use of unsaturated nitrogen containing compounds including bipyridyl compounds as internal electron donor or as SCA. US Patent No 6,399,837 of Wilson et al describes the use of 1-ethoxy-2-n-alkoxybenzene compounds as internal electron donor or as SCA or as both.

There is described in our PCT publication No WO 02/44220A1 a lower alpha alkene polymerisation heterogeneous solid catalyst comprising a hydrated magnesium chloride derived procatalyst comprising a titanium tetrahalide supported on a magnesium chloride ester complex precursor. The internal electron donor ester component of the precursor is generated insitu by reaction of a magnesium chloride alcoholate with an activated carbonyl compound in the mole ratio 0.5 - 1 : 10 - 20.

The magnesium chloride alcoholate is formed of hydrated magnesium chloride and an aliphatic alcohol in the mole ratio of 0.5 - 1 : 10 - 20. The catalyst comprises a cocatalyst comprising an organoaluminium compound, the mole ratio of the aluminium to the titanium being 10 - 300 : 1. The catalyst also comprises a selectivity control agent comprising an ester or ether in the mole ratio 10 - 100 : 1 with respect to the titanium.

There is described in our PCT Publication No WO 03/62283 an olefin polymerisation titanium catalyst comprising a titanium compound and an organoaluminium compound cocatalyst supported on a soluble polysulfone comprising free reactive sulfone groups. The molar ratio of titanium to aluminium is 1-10 : 200 and the weight ratio of titanium to polysulfone is 0.01 - 0.1 : 0.3 - 2.5.

There is described in our PCT application No PCT/IN03/00152 a single step process for the preparation of lower alpha alkene polymerisation heterogeneous solid catalyst comprising an organomagnesium precursor derived procatalyst comprising magnesium chloride supported titanium chloride and an internal electron donor and an organoaluminium compound based cocatalyst. The procatalyst is obtained by single step reaction under microwave irradiation of 300 to 1200 W.

Selectivity control Agents reported in the prior art invariably have an aromatic ring and many aromatic compounds are known to be toxic and/or having other undesirable properties.

The cocatalyst is organoaluminium compound such as trialkyl aluminium or dialkyl aluminium halide. The alkyl group may be methyl, ethyl, butyl, isobutyl, hexyl and

octyl and the halide may be chloride or bromide. The preferred cocatalyst is triethyl aluminium..

OBJECTS OF INVENTION

5 An object of the invention is to provide a catalytic system for polymerisation of lower alpha alkene comprising SCA which is non-toxic and without side effects.

10 Another object of the invention is to provide a catalytic system for polymerisation of lower alpha alkene which shows high activity and selectivity.

 Another object of the invention is to provide a catalytic system for polymerisation of lower alpha alkene which is economical.

15 Another object of the invention is to provide a process for the preparation of a catalytic system for polymerisation of lower alpha alkene comprising SCA which is non-toxic and without side effects.

20 Another object of the invention is to provide a process for the preparation of a catalytic system for polymerisation of lower alpha alkene, which shows high activity and selectivity.

 Another object of the invention is to provide a process for the preparation of a catalytic system for polymerisation of lower alpha alkene, which is economical.

Another object of the invention is to provide a process for the polymerisation of lower alpha alkene using a catalytic system, comprising SCA which is non-toxic and without side effects.

5 Another object of the invention is to provide a process for the polymerisation of lower alpha alkene using a catalytic system, which shows high activity and selectivity.

10 Another object of the invention is to provide a process for the polymerisation of lower alpha alkene using a catalytic system, which is economical.

DETAILED DESCRIPTION OF INVENTION

15 According to the invention there is provided a catalytic system for polymerisation of lower alpha alkene consisting of an organomagnesium or magnesium chloride derived procatalyst consisting of magnesium chloride supported titanium chloride and an internal electron donor and an organoaluminium based cocatalyst and a selectivity control agent, wherein the selectivity control agent consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R) - dihydroxy-butane-1,4-
20 dicarboxylic acid or (2-S, 3-S)- dihydroxybutane-1,4-dicarboxylic acid, the molar ratio of the optically pure isomers of the tartrates to titanium being .0375 to 1.5.

25 According to the invention there is also provided a process for the preparation of a catalytic system for polymerisation of lower alpha alkene consisting of mixing an organomagnesium or magnesium chloride derived procatalyst consisting of magnesium chloride supported titanium chloride and an internal electron donor and an

organoaluminium based cocatalyst and a selectivity control agent, wherein the selectivity control agent consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R)-dihydroxy-butane-1, 4-dicarboxylic acid or (2-S, 3-S)-dihydroxybutane-1, 4-dicarboxylic acid, the molar ratio of the optically pure isomers of the tartrates to titanium being .0375 to 1.5.

According to the invention there is also provided a process for the polymerisation of lower alpha alkene consisting of reacting the lower alpha alkene with a catalytic system consisting of an organomagnesium or magnesium chloride derived procatalyst consisting of magnesium chloride supported titanium chloride and an internal electron donor and an organomagnesium based cocatalyst and a selectivity control agent, wherein the selectivity control agent consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R)-dihydroxy-butane-1, 4-dicarboxylic acid or (2-S, 3-S)-dihydroxybutane-1, 4-dicarboxylic acid, the molar ratio of the optically pure isomers of the tartrates to titanium being .0375 to 1.5 under polymerisation conditions in known manner.

Preferably, the molar ratio of the optically pure isomers of the tartrates to titanium is 0.7.

Preferably the tartrates are alkyl or cycloalkyl esters of (2-R, 3-R)-dihydroxybutane-1,4-dicarboxylic acid.

The polymerisation of the lower alpha alkene using the catalyst of the invention is carried out in a known manner for instance polymerisation may be carried out in gas phase employing one or more fluidised beds of the catalyst. Alternatively it may also be conducted in a slurry phase in the presence of an inert hydrocarbon diluent like

toluene or hexane. The constituents of the polymerisation catalyst may be mixed in a vessel outside the polymerisation reactor and then transferred therein. Alternatively they may be mixed together in the reactor to form the catalyst insitu.

5 The invention is described with reference to the following example which is intended to illustrate and not to limit the scope of invention.

Example

10 Polymerization reactions were carried in the slurry phase with hexane as the diluent under a constant pressure of 5 kg for 1 hr at 70°C as per the polymerisation data as given in the following Table. The procatalyst (0.1 GM) was mixed with triethyl aluminium co-catalyst (1.425 GM) and SCA in the amount indicated in the following Table:

Table

Internal Electron Donor of the Procatalyst	SCA (2-R,3-R)-dihydroxybutane-1,4-dicarboxylic acid Alkyl =	Polypropylene yield (KG per GM of procatalyst); Selectivity (Xylene soluble %)
Ethyl benzoate	None	4.0; 93
	Di-n-propyl	3.5; 95
Ethyl benzoate	Di-isopropyl	4.3; 93
	Di-2-ethylhexyl	3.7; 95
	Di-n-propyl	3.8; 94
Di-isobutyl phthalate	Di-isopropyl	4.0; 93
	Di-2-ethylhexyl	3.7; 95
	Di-n-propyl	3.7; 94

The Table clearly indicates that the catalytic system of the invention has excellent activity and selectivity for the polymerisation of polypropylene. According to the invention the selectivity control agent comprises naturally derived optically pure isomers of tartrates which are non-toxic and without side effects besides being economical.

5

1) Catalytic system for polymerisation of lower alpha alkene consisting of an organomagnesium or magnesium chloride derived procatalyst consisting of magnesium chloride supported titanium chloride and an internal electron donor and an organoaluminium based cocatalyst and a selectivity control agent, wherein the selectivity control agent consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R) - dihydroxy-butane-1,4-dicarboxylic acid or (2-S, 3-S)-dihydroxybutane-1,4-dicarboxylic acid, the molar ratio of the optically pure isomers of the tartrates to titanium being .0375 to 1.5.

2) Catalytic system as claimed in claim 1, wherein the molar ratio of the optically pure isomers of the tartrates to titanium is 0.7.

3) Catalytic system as claimed in claim 1, wherein the tartrates are alkyl or cyclo alkyl esters of (2-R, 3-R)-dihydroxybutane-1,4-dicarboxylic acid.

4) Process for the preparation of a catalytic system for polymerisation of lower alpha alkene consisting of mixing an organomagnesium or magnesium chloride derived procatalyst consisting of magnesium chloride supported titanium chloride and an internal electron donor and an organoaluminium based cocatalyst and a selectivity control agent, wherein the selectivity control agent consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R)-dihydroxy-butane-1, 4-dicarboxylic acid or (2-S, 3-S)-dihydroxybutane-1, 4-dicarboxylic acid, the molar ratio of the optically pure isomers of the tartrates to titanium being .0375 to 1.5.

5) Process as claimed in claim 4, wherein the molar ratio of the optically pure isomers of the tartrates to titanium is 0.7.

6) Process as claimed in claim 4, wherein the tartrates are alkyl or cyco alkyl esters of (2-R, 3-R)- dihydroxybutane-1,4-dicarboxylic acid.

7) Process for the polymerisation of lower alpha alkene consisting of reacting the lower alpha alkene with a catalytic system consisting of an organomagnesium or magnesium chloride derived procatalyst consisting of magnesium chloride supported titanium chloride and an internal electron donor and an organomagnesium based cocatalyst and a selectivity control agent, wherein the selectivity control agent consists of naturally derived optically pure isomers of tartrates such as esters of (2-R, 3-R)-dihydroxy-butane-1, 4-dicarboxylic acid or (2-S, 3-S)-dihydroxybutane-1, 4-dicarboxylic acid, the molar ratio of the optically pure isomers of the tartrates to titanium being .0375 to 1.5, under polymerisation conditions in known manner.

8) Process as claimed in claim 7, wherein the molar ratio of the optically pure isomers of the tartrates to titanium is 0.7.

9) Process as claimed in claim 7, wherein the tartrates are alkyl or cyco alkyl esters of (2-R, 3-R)-dihydroxybutane-1, 4-dicarboxylic acid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN 2004/000043

A. CLASSIFICATION OF SUBJECT MATTER C 08 F 4/654, 10/00 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B 01 J, C 08 F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPODOC, WPI, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 45977 A2 (MONTEDISON S.p.A.) 17 February 1982 (17.02.1982). <i>claims 1&2.</i>	1-9
	--	
A	US 5436213 A (IISKOLA et al.) 25 July 1995 (25.07.1995) <i>claim 1.</i>	1-9
	--	
A	US 5166113 A (SCHWAGER et al.) 24 November 1992 (24.11.1992) <i>claim 1.</i>	1-9
	--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 July 2004 (26.07.2004)		Date of mailing of the international search report 7 September 2004 (07.09.2004)
Name and mailing address of the ISA/ AT Austrian Patent Office Dresdner Straße 87, A-1200 Vienna Facsimile No. +43 / 1 / 534 24 / 535		Authorized officer PUSTERER F. Telephone No. +43 / 1 / 534 24 / 311

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN 2004/000043

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4725656 A (KASHIWA et al.) 16 February 1988 (16.02.1988) <i>claim 1.</i>	1-9
A	-- US 5227438 A (REBAN) 13 July 1993 (13.07.1993) <i>claim 1; column 3, lines 22-39.</i> -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/IN 2004/000043

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
EP	A	45977		US	B	6777508	2004-08-17
				US	B	6515085	2003-02-04
				YU	B	42419B	1988-08-31
				YU	B	42418B	1988-08-31
				YU	A	195781	1983-10-31
				US	B	6194342	2001-02-27
US	A	4725656	1988-02-16	DE	D	3381910D	1990-10-31
				AT	T	56981T	1990-10-15
				US	A	5075396	1991-12-24
				US	A	4841003	1989-06-20
				EP	A	0115195	1984-08-08
US	A	5166113	1992-11-24	BR	A	9005591	1991-09-17
				ZA	A	9008839	1992-07-29
				AT	T	99334T	1994-01-15
				ES	T	2047229T	1994-02-16
				EP	A	0427060	1991-05-15
US	A	5227438	1993-07-13	EP	A	0534405	1993-03-31
				JP	A	5202103	1993-08-10
US	A	5436213	1995-07-25	NO	A	932008	1993-07-12
				ES	T	2104944T	1997-10-16
				FI	A	914627	1993-04-03
				DE	T	69219755T	1997-10-09
				DE	D	69219755D	1997-06-19